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Studies of the Ruthenium(III) Complex. V. Aquation and Anation Reactions of Halogenoacetatopentaammineruthenium(III) Complexes in Aqueous Solutions

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The kinetics of aquation and anation reaction have been studied with pentaamineruthenium(III) complexes containing halogenoacetates (fluoro-, monochloro-, dichloro-, trichloro-, bromo-, and iodoacetates). It has been found that the aquation reaction proceeds through two kinds of paths, *i.e.* the acid-catalysed path and the acid-uncatalysed path, except the cases of dichloro- and trichloroacetate complexes. The aquations of dichloro- and trichloroacetate complexes are not catalysed by a proton because these ligand acids are strong acids. The equilibrium constants between $[RuH_2O(NH_3)_5]^{3+}$ and $[RuO_2CRX(NH_3)_5]^{2+}$ (O_2CRX=halogenoacetate), K_{eq}, were calculated from the anation and aquation rate constants. The k_{aq} and K_{eq} values for the fluoro-, chloro-, dichloro-, trichloro-, bromo-, and iodoacetatocomplexes are, respectively: k_{aq}, 10×10^{-5}, 7.5×10^{-5}, 19.1×10^{-5}, 49.0×10^{-5}, 6.8×10^{-5} and 6.7×10^{-5} sec^{-1}; K_{eq}, 5.2×10^{-3}, 3.6×10^{-3}, 9.0×10^{-3}, 23×10^{-3}, 3.5×10^{-3}, and 3.3×10^{-3} M, at 60 °C. The free energy plot, log k_{aq} *vs.* log K_{eq}, gave a straight line with a gradient of 1.0. It has been concluded that the acid-uncatalysed reaction proceeds via a S_N1 mechanism, while the acid-catalysed reaction seems to take place with a S_N2 mechanism. Some remarks have been made on the molecular interaction between the complex and the acid catalyst.

In a previous paper we reported on the kinetics of acid-hydrolysis for carboxylatopentaammineruthenium(III) complexes.[1] It was found that one of the reaction paths, *i.e.*, the acid-uncatalysed one, proceeded through a dissociative mechanism; however, the mechanism for the acid-catalysed path was not clear. We have now extended the study to obtain further information concerning the reaction mechanism. Thus, the aquation and anation rate constants were measured, and the reaction mechanisms were discussed on the basis of the free-energy relationship.[2]

Experimental

Materials. All the chemicals used were of a reagent grade. Twice-distilled water was used in all kinetic runs. The ionic strength and the acidity of the reaction solution were adjusted with *p*-toluenesulphonic acid and its sodium salt.

Chloropentaammineruthenium (III) chloride was prepared by the method of Allen *et al.*[3),4)] from ruthenium trichloride and hydrazine hydrate.

Found: H, 5.08; N, 23.75%. Calcd for $[RuCl(NH_3)_5]Cl_2$: H, 5.19; N, 23.98%.

Aquopentaammineruthenium(III) perchlorate was prepared by the method of Endicott and Taube.[5]

Found: H, 3.20; N, 13.74%. Calcd for $[Ru(H_2O)(NH_3)_5](ClO_4)_3$: H, 3.42; N, 13.94%.

Halogenoacetatopentaammineruthenium(III) perchlorates were prepared by the method of Stritar and Taube[6] from chloropentaammineruthenium chloride, a halogenoacetate buffer solution, and a zinc amalgam.

Found: C, 5.06; H, 3.40; N, 15.00%. Calcd for $[RuO_2CCH_2F(NH_3)_5](ClO_4)_2$: C, 5.19; H, 3.68; N, 15.15%.

Found: C, 4.77; H, 3.50; N, 14.86%. Calcd for $[RuO_2CCH_2Cl(NH_3)_5](ClO_4)_2$: C, 5.02; H, 3.59; N, 14.63%.

Found: C, 4.73; H, 3.18; N, 13.73%. Calcd for $[RuO_2CCHCl_2(NH_3)_5](ClO_4)_2$: C, 4.68; H, 3.12; N, 13.65%.

Found: C, 4.58; H, 2.86; N, 12.83%. Calcd for $[RuO_2CCCl_3(NH_3)_5](ClO_4)_2$: C, 4.39; H, 2.74; N, 12.79%.

Found: C, 4.40; H, 3.08; N, 13.14%. Calcd for $[RuO_2CCH_2Br(NH_3)_5](ClO_4)_2$: C, 4.59; H, 3.25; N, 13.38%.

Found: C, 4.30; H, 2.85; N, 12.17%. Calcd for $[RuO_2CCH_2I(NH_3)_5](ClO_4)_2$: C, 4.21; H, 2.98; N, 12.28%.

Kinetic Runs. The aquation rate was measured spectrophotometically as previously has been described.[1] The rate of anation is expressed by the ordinary second-order rate formula:

$$dx/dt = k_{an}(a-x)(b-x) - k_{aq}x \qquad (1)$$

where x is the concentration of the $[RuO_2CRX(NH_3)_5]^{2+}$ ion at time t, and where a and b are the initial concentrations of $[RuH_2O(NH_3)_5]^{3+}$ and the halogenoacetate ion respectively. The last is known from the formal concentration and the acid dissociation constant under the given conditions. When the value of a is negligibly small as compared with b, Eq. (1) can be integrated to give;

$$\ln[(x_\infty - x)/x_\infty] = -(k_{aq}+bk_{an})t \qquad (2)$$

where the suffix ∞ denotes the equilibrated state. When the anation is measured by a spectrophotometric method, Eq. (2) is replaced by;

$$\ln[(A_\infty - A_t)/(A_\infty - A_0)] = -(k_{aq}+bk_{an})t \qquad (3)$$

where A_0, A_t, and A_∞ are the extinctions of the reaction mixture in the initial state, at time t, and in the final state respectively. By plotting $\log(A-A_t)$ vs. t, the apparent rate constant, k_{obs}, can be obtained. The equilibrium quotient, K_{eq}, was calculated from the value of k_{aq} and k_{an}.

Results and Discussion

Aquation Reactions. The pseudo first-order rate constants, k_{obs}, for the aquation of complexes were measured at different hydrogen-ion concentrations of the reaction solution. As is illustrated in Fig. 1, the plots of k_{obs} *vs.* the hydrogen-ion concentration gave straight lines for all the complexes. The observed rate constant, k_{obs}, can be expressed by Eq. (4);

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1) A. Ohyoshi, A. Jyo, and N. Shin, This Bulletin, **45**, 2121 (1972).

2) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

3) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967).

4) A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337 (1967).

5) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **84**. 4984 (1962).

6) J. A. Stritar and H. Taube, *Inorg. Chem.* **8**, 2281 (1969).

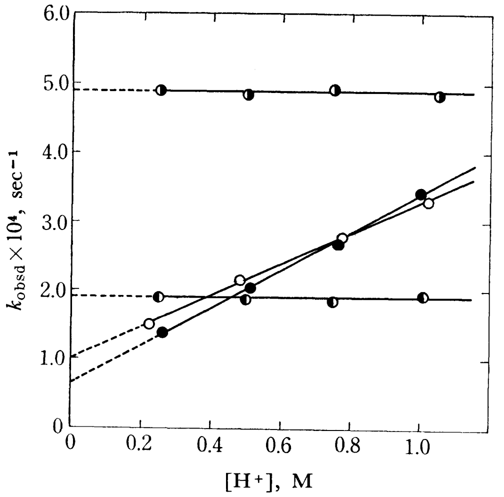


Fig. 1. Relationship between k_{obs} of aquation reaction and the hydrogen-ion concentration. (60 °C, $\mu=1.0$)
○ fluoroacetato-, ● iodoacetato-, ◐ dichloroacetato-, ◑ trichloroacetato- complex.

$$k_{obs} = k_{H_2O} + k_H[H^+] \quad (4)$$

where k_{H_2O} is the acid-independent rate constant and where k_H is the acid-dependent rate constant. In the cases of dichloro- and trichloro-acetatocomplexes, the contribution of the k_H path in Eq. (4) was negligible compared with the k_{H_2O} path; therefore, the rate constant of aquation, k_{aq} could be approximated as equal to k_{H_2O}. The calculated k_{H_2O} and k_H values are listed in Table 1, together with the pK_a values of the ligand acids.

Table 1. Rate constants of acid-catalysed and uncatalyzed paths in the aquation reaction of halogenoacetatopentaammineruthenium(III) complexes at $\mu=1.0$

Complexes	temp. °C	pK_a [a] (35 °C)	$k_{H_2O}\times 10^4$, sec^{-1}	$k_H\times 10^4$, M^{-1}sec^{-1}
Fluoroacetato-	40.1	2.624	0.1	0.25
	50.0		0.28	0.82
	60.0		1.0	2.3
	70.0		1.4	7.9
Chloroacetato-	40.0	2.90	0.05	0.44
	50.3		0.17	1.41
	59.8		0.75	2.50
	70.4		1.48	8.4
Bromoacetato-	40.3	2.94	0.10	0.50
	50.0		0.14	1.45
	60.0		0.68	2.6
	69.5		1.7	8.5
Iodoacetato-	40.2	3.21	0.04	0.86
	49.6		0.13	1.50
	60.2		0.67	2.7
	71.8		1.4	8.7
Dichloroacetato-	60.0	1.32	1.91	—
Trichloroacetato-	60.1	0.70	4.90	—

a) These values obtained from Ref. 7.

The rates of aquation increase with an increase in the ionic strength. Applying the Brønsted-Bjerrum-Christiansen formulation[8] (Eq. 5), the dependence of the ionic strength on the k_H value was investigated.

$$\ln k_H = \ln k_{H,0} + \frac{2AZ_1Z_2\sqrt{\mu}}{1+B\sqrt{\mu}} \quad (5)$$

where k_H is the acid-dependent rate constant, $k_{H,0}$ is the same for infinite dilution, Z_1 and Z_2 are the charges on the two reactants, μ is the ionic strength, A is a constant equal to 0.509 for water at 25 °C, and the B constant is of the order of the magnitude of unity.

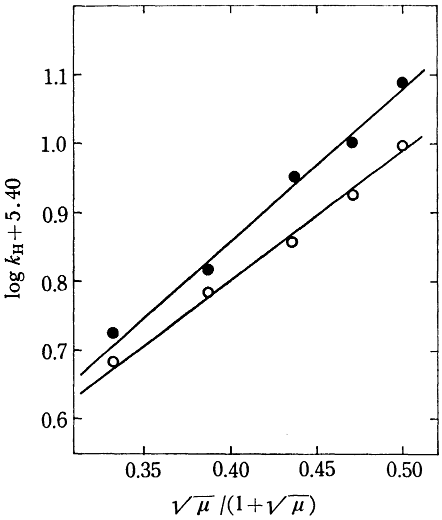
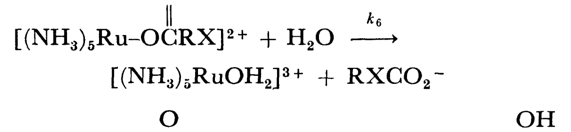
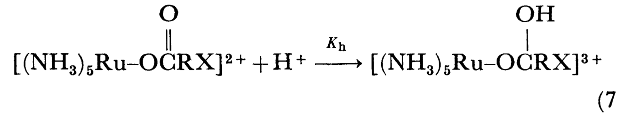


Fig. 2. Relationship between the acid-catalysed rate constant k_H and the ionic strength of the solution. (60 °C, [H$^+$]=0.025 M)
○ Fluoroacetato complex, ● Iodoacetato complex
temp: 60 °C, [H$^+$]=0.025 M

Figure 2 shows the relationship; between the k_H values and μ according to the simplified equation, Equation (5). Since the present experiment was carried out at $\mu=1.0$, this relationship is not sufficiently reliable; however, the slopes of the straight lines in Fig. 2 are both nearly +2, and these facts suffice to show the role of the proton at the transition state in the acid-dependent path. These results show that the aquation rate of the complex is dependent on the hydrogen-ion concentration and that the two reaction paths are involved in the reaction. This can be expressed by Eq. (6) for one path and by Eqs. (7) and (8) for the other path:



$$[(NH_3)_5Ru\text{-}O\overset{\overset{O}{\|}}{C}RX]^{2+} + H_2O \xrightarrow{k_6} [(NH_3)_5RuOH_2]^{3+} + RXCO_2^- \quad (6)$$



$$[(NH_3)_5Ru\text{-}O\overset{\overset{O}{\|}}{C}RX]^{2+} + H^+ \xrightarrow{K_h} [(NH_3)_5Ru\text{-}O\overset{\overset{OH}{|}}{C}RX]^{3+} \quad (7)$$

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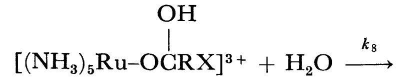
7) G. Kortüm, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acid in Aqueous Solution," Butterworths, London (1961), p. 291—295.

8) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., John Wiley and Sons Inc., New York (1967), p. 34.



$$[(NH_3)_5Ru\text{-}O\overset{OH}{\overset{|}{C}}RX]^{3+} + H_2O \xrightarrow{k_8} [(NH_3)_5RuOH_2]^{3+} + RXCO_2^- + H^+ \qquad (8)$$

The rate constant of the uncatalysed path (Eq. (6)), k_6 corresponds to k_{aq}. Equations (7) and (8) indicate the acid-catalysed path, the rate constant, k_H, of which can be expressed by Equation (9);

$$k_H = k_8 K_h \qquad (9)$$

This relationship for the hydrolysis of similar complexes of Co(III), Rh(III), and Ir(III) has previously been reported.[9–13]

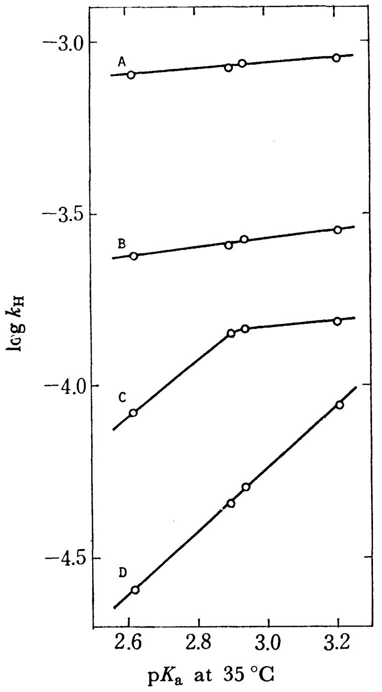
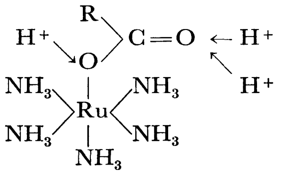


Fig. 3. Relationship between k_H of aquation reactions and pK_a of the ligand acids.
A: 70 °C, B: 60 °C, C: 50 °C, D: 40 °C

As is shown in Fig. 3, the plot of log k_H *vs.* the pK_a value of the ligand acid gives a straight line, with a gradient almost unity at lower reaction temperatures, while the gradient is about zero at higher temperatures, therefore, the weak acid seems to behave as the strong acid. The smaller k_H values of fluoroacetatocomplex compared to these of the iodoacetatocomplex (Table 1) may be due to the smaller tendency of forming a protonated intermediate shown by Eq. (7); that is, the electrostatic effect of the halogen atom is reflected in the constant, K_h, of Eq. (7), which is important in determining the k_H values.

Some remarks should be made here on the molecular interaction between carboxylatopentaammineruthenium(III) complexes ($(NH_3)_5RuOC(=O)R^{2+}$) and the acid catalyst, H^+. Three distinctive modes of interaction can be allowed in view of the orbital symmetry and orbital energies of the two species:



Ru–O=2.5 Å; Ru–N=2.23 Å; N–H=1.031 Å; C–O=1.28—1.43 Å, ∠RuOC=105°; ∠OCO=122.4—130°

The preliminary calculations of the all-valence-shell-electron extended Hückel MO on the above interacting system of $(NH_3)_5RuOC(=O)R^{2+}$—H^+[14] have demonstrated that the most plausible interaction of the H^+ catalyst occurs predominantly in the direction of the orbital expansion of the nonbonding lone-pair 2p-orbital on the oxygen atom of the Ru–O bond in terms of the weakening of the Ru–O; in the case of $(NH_3)_5RuOC(-O)H^{2+}$, the bond population of Ru–O (0.085) is lessened to 0.073 by the electrophilic attack of the H^+ catalyst (H^+—O≳0.97 Å).

It is worthy of emphasis that the single C–O bond is not weakened by the attack of the catalyst and that, in some measure, the solvent of H_2O participates in the weakening of the Ru–O bond; the details of this will be discussed precisely in a succeeding paper.

As is shown in Table 1, an antiparallel relationship is found between the k_{H_2O} values and the pK_a values of the halogenocarboxylic acids. Similar results were obtained for the carboxylato-[9] and amino acido-[13] pentaamminecobalt(III), and analogous ruthenium(III) complexes.[1] These results indicate that the aquation takes place via the S_N1 (lim) mechanism because the rupture of the metal-ligand bond depends on the bond strength predicted by the pK_a of the carboxylic acids.

Anation Reactions and the Free-Energy Relationship. The anation reaction of aquopentaammineruthenium (III) complexes with halogenoacetate ions may be written as;

$$[RuH_2O(NH_3)_5]^{3+} + RXCOO^- \rightleftarrows [RuO_2CRX(NH_3)_5]^{2+} + H_2O \qquad (10)$$

and the rate constant, k_{obs}, may be expressed by the following equation;

$$k_{obs} = k_{aq} + k_{an}[RXCOO^-] \qquad (11)$$

The k_{an} is obtained from the slope of the linear plot of k_{obs} vs. $[RXCOO^-]$, as is shown in Fig. 4. The equilibrium quotient, K_{eq}, is expressed by:

$$K_{eq} = k_{aq}/k_{an} \qquad (12)$$

The values of k_{an} and K_{eq} are listed in Table 3.

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[9] F. Basolo, J. G. Bergmann, and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952).

[10] F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

[11] K. Kuroda, *Nippon Kagaku Zasshi*, **82**, 572 (1961).

[12] K. Ogino, T. Murakami, and K. Saito, This Bulletin, 41, 1615 (1968).

[13] T. Murakami, K. Ogino, H. Kobayashi, H. Yamazaki, and K. Saito, *ibid.*, **44**, 120 (1971).

[14] The Coulomb integrals for the s, p, and d orbitals of Ru were taken to be −9.00 eV, −7.00 eV, and −12.00 eV respectively, on the basis of L. L. Lohr, Jr., and W. N. Lipscomb, *Inorg. Chem.*, **3**, 22 (1964), and those for the s and p orbitals of the other atoms were supplied by J. Hinze and H. H. Jaffè, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

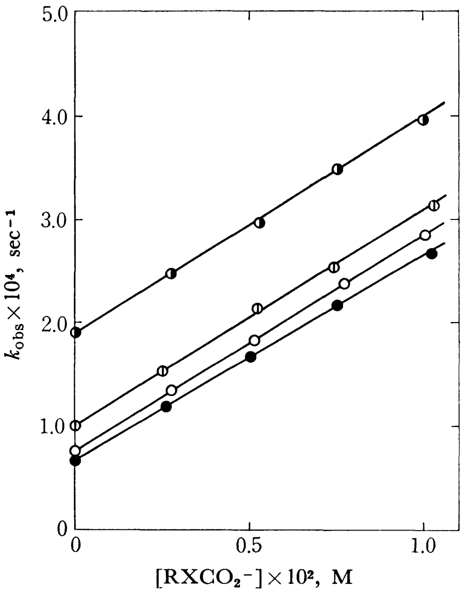

Fig. 4. Relationship between the k_{obs} of anation reaction and the concentration of halogenoacetate ion. (60 °C, $\mu=0.1$)
● iodoacetato-, ○ chloroacetato-, ⦶ fluoroacetato, ◑ dichloroacetato-complex

Table 2. Rate constants of aquation and anation, and equilibrium quotients of aquation-anation reactions of halogenoacetatopentaammineruthenium(III) complexes

Complexes	$k_{an}\times10^2$, M^{-1} sec^{-1}	$k_{aq}\times10^5$, sec^{-1}	$K_{eq}\times10^3$, M
Fluoroacetato-	2.1	10	4.8
Chloroacetato-	2.1	7.5	3.6
Bromoacetato-	1.9	6.8	3.5
Iodoacetato-	2.0	6.7	3.3
Dichloroacetato-	2.1	19.1	9.0
Trichloroacetato-	2.1	49.1	23

Langford[2], Haim[15] and Murakami *et al.*[13] examined the linear free-energy relationship between the equilibrium quotient and the rate constant for aquation reactions of various acidopentaamminecobalt(III) complexes and obtained a gradient unity in their log-log plot;

$$\Delta \ln k_{aq} = \alpha\Delta \ln K_{eq} \tag{13}$$

This value suggests a similarity between the transition state and the product. When this value is unity, the state of the ligand is the same as that in the product.

A similar plot of our results for the halogenoacetatopentaammineruthenium(III) complexes is shown in Fig. 5. An apparent α value of 1.0 is obtained from the gradient of the straight line. Thus, it can be concluded that the halogenoacetate ligand in the transition state for the aquation reaction is very similar to solvated anions; that is, the aquation reaction proceeds by the S_N1 mechanism.

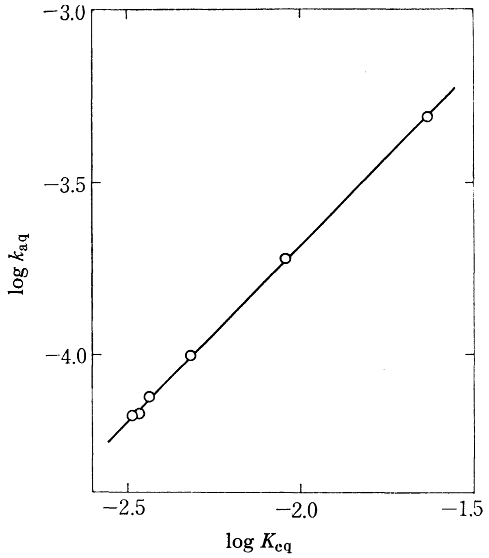

Fig. 5. Linear free energy relationship between the equilibrium quotient K_{eq} and the rate constant for aquation, k_{aq}.
Least-squares equation $\log k_{aq}=-1.63+1.02 \log K_{eq}$

Haim[15] gives Eq. (14) in discussing the relation between k_{aq} and K_{eq} for the auqations of the pentaammine series of cobalt(III) complexes:

$$\log k_{aq} = \log k_xK_0 - \log K_{eq} \tag{14}$$

where K_0 is the ion-pair or outer-sphere complex formation constant between the aquopentaammine ion and the incoming ligand, and k_x, the inner sphere-outer sphere interchange velocity of the ion pair.

In the present study, a similar discussion is possible for the anation and aquation mechanisms. Since $K_{eq}=K_0k_x/k_{aq}$, the gradient of 1.0 in the $\log k_{aq}$ *vs.* $\log K_{eq}$ plot (Fig. 5) implies that the first term on the right-hand side of Equation (14) is independent of the nature of the incoming ligand, $RXCO_2^-$, in Reaction (10). The $\log k_xK_0$ term will be constant if the individual values of k_x and K_0 remain constant as the ligand $RXCO_2^-$ is varied. Since the value of K_0 is determined by the charge of the ligand, Langford's linear correlation for the $RXCOO^-$ ligands implies that the values of k_x are independent of the nature of the ligand. As is shown in Table 2, the observed rate constants for various anation reactions are practically the same; that is, there is little assistance by the incoming ligand in the outer sphere-inner sphere interchange reaction. In other words, this interchange is the rate-determining step for the anation reaction.

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[15] A. Haim, *Inorg. Chem.*, **9**, 426 (1970).